

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-058100

(43)Date of publication of application : 03.03.1995

(51)Int.Cl.

H01L 21/316  
C23C 16/50  
H01L 21/205  
H01L 21/31

(21)Application number : 05-198369

(71)Applicant : KAWASAKI STEEL CORP

(22)Date of filing : 10.08.1993

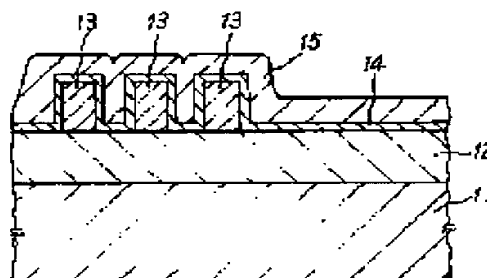
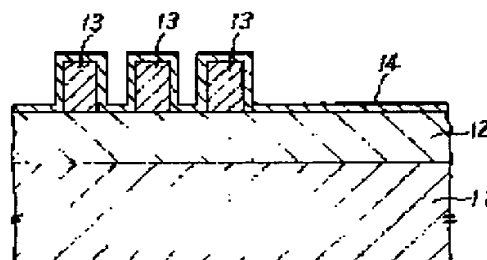
(72)Inventor : SATO NOBUYOSHI  
NAKANO TADASHI  
OOTA TOMOHIRO

## (54) MANUFACTURE OF SEMICONDUCTOR DEVICE

## (57)Abstract:

PURPOSE: To provide the manufacturing method of a semiconductor device, which has the excellent film quality and has the excellent embedding performance into the step and flatness.

CONSTITUTION: The ratio of oxygen/TEOS is set at 2 or more. A first insulating film 14 is formed by plasma CVD. Then, a substrate is processed with processing fluid containing organic compound. Thereafter, a second insulating film 15 is formed by chemical vapor growth.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] Plasma CVD which makes an organic silane and oxygen material gas It hits forming the insulator layer of a semiconductor device on the formed insulator layer by the chemical vapor deposition which makes an organic silane material gas, and is the aforementioned plasma CVD. The ratio of the oxygen and the organic silane which can be set is made or more into two, and it is plasma CVD. The manufacture method of the semiconductor device characterized by forming the account insulator layer of back to front which processed the front face of the formed insulator layer by the processing fluid containing an organic compound by the chemical vapor deposition.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the method of forming the last insulator layer which acts as the manufacture method of a semiconductor device especially the primary insulator layer between a semiconductor base and the 1st layer metal wiring, the layer insulation film during metal wiring, and a passivation film, and the insulator layer which can be used as a sidewall of the gate of a field-effect transistor by the chemical vapor deposition.

[0002]

[Description of the Prior Art] In recent years, high integration of a VLSI device and densification progress quickly, and semiconductor processing technology is becoming what has indispensable submicron lithography. Submicron lithography follows on progressing, the irregularity of a semiconductor base front face becomes still more intense, an aspect ratio becomes large, and this irregularity is becoming the restrictions on device manufacture. The flattening technology of a layer insulation film is wished most strongly because of solution of such a problem.

[0003] The method of forming an insulator layer by plasma-TEOS CVD on a semiconductor base, and forming an insulator layer by ozone-TEOS CVD on this insulator layer as the formation method of the layer insulation film which fills such a demand, is learned. By the formation method of this insulator layer, in order to improve embedded nature generally, on the occasion of formation of the plasma-TEOS insulator layer used as a ground, the ratio of oxygen and TEOS sets or less to one, and film formation is performed.

[0004]

[Problem(s) to be Solved by the Invention] If the ratio of oxygen/TEOS is made or less into one in case an insulator layer is formed by plasma-TEOS CVD, un-arranging [ for which a lot of moisture and carbon remain in the film with which the membraneous quality formed since the partial pressure of oxygen is small is formed bad ] will arise. Consequently, the membraneous quality of the ozone-TEOS CVD film formed on it was also bad, and, moreover, there was a difficulty also in the embedded nature and flat nature of an ozone-TEOS film by the ground dependency.

[0005] The method of forming an ozone-TEOS CVD film by this application people, as a method of canceling such a fault, after processing a ground front face by the processing fluid containing an organic compound is proposed. When the formation method of this insulator layer reduces a ground dependency and embedded nature is improved, a very useful effect is attained. However, when the partial pressure of oxygen is small in formation of a plasma-TEOS CVD film, for a low reason, there is a possibility that the effect according [ the density of the adsorption site of the silanol on the front face of a ground ] to organic compound processing may not fully be demonstrated.

[0006] Therefore, the purpose of this invention is to propose the manufacture method of a semiconductor device of having improved the treatment effect by the organic compound further, and having improved further the generating prevention of embeddability or a void between level differences.

[0007]

[Means for Solving the Problem] The manufacture method of the semiconductor device by this invention is plasma CVD which makes an organic silane and oxygen material gas. It hits forming the insulator layer of a semiconductor device on the formed insulator layer by the chemical vapor deposition which makes an organic silane material gas, and it is the aforementioned plasma CVD. The ratio of the oxygen and the organic silane which can be set is made or more into two, and it is plasma CVD. It is characterized by to form the account insulator layer of back to front which processed the front face of the formed insulator layer by the processing fluid In this invention, it is suitable to form the aforementioned insulator layer by the chemical vapor deposition using an organic silane as a raw material. As this organic silane, they are TEOS mentioned above, for example, TMOS, OMCTS, HMDS, start of block, and DADBS. Or SOP Although it can carry out, also let other silane compounds be raw materials. Furthermore, it sets to the manufacture method of the semiconductor device by this invention, and they are OH basis, CO machine, and COC about the organic compound of the aforementioned processing fluid. A machine, CN basis, and NO<sub>2</sub> It is suitable to consider as the organic compound or heterocyclic compound which has a machine and at least one sort of functional groups of the NR (s) (R=H or alkyl group). It is suitable to consider as the alcohol which has OH basis among these organic compounds especially ethanol, or a methanol. Moreover, the solution or the organic-solvent solution of an organic compound can also be used as a processing fluid. Furthermore, like the example mentioned later, before forming an insulator layer by the chemical vapor deposition, a ground insulator layer can be formed, this ground insulator layer can be processed by the processing fluid, or a polysilicon party turn can be formed, and the front face can be processed by the processing fluid.

[0008] As mentioned above, as an organic compound for performing surface treatment, aliphatic saturation monohydric alcohol, aliphatic unsaturation monohydric alcohol, aromatic alcohols, aliphatic saturation polyhydric alcohol and the derivative of those, an aldehyde, the ether, a ketone keto alcohol, a carboxylic acid, a nitroalkane, an amine, acyl nitril, an acid amide, and a heterocyclic compound are mentioned, and the following matter can be used concretely.  
 Aliphatic saturation monohydric alcohol (OH machine) : [ A methanol, ethanol, ] 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, 2-methyl-2-propanol, 1-pentanol, A 3-methyl-1-butanol, a 3-methyl-2-butanol, a 2-methyl-2-butanol, 1-hexanol and cyclohexanol  
 aliphatic unsaturation monohydric alcohol (OH machine) : [ Allyl alcohol, ] Propargyl alcohol and 2-methyl-3-butyne-2-ol  
 aromatic alcohols (OH machine) : [ Benzyl alcohol, ] Furfuryl alcohol  
 aliphatic saturation polyhydric alcohol and derivative of those (OH machine) : [ Ethylene glycol, ] A propylene glycol, a diethylene glycol, an ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, an ethylene glycol monochrome n butyl ether, The ethylene glycol monochrome isobutyl ether, a propylene glycol monomethyl ether, An ethylene glycol wood ether, the diethylene-glycol monomethyl ether, A diethylene glycol monoethyl ether, diethylene-glycol wood-ether  
 aldehyde (CO machine) : [ Formaldehyde, ] An acetaldehyde, the glyoxal ether (COC basis) : [ Diethylether, ] A dioxane, a tetrahydrofuran, tetrahydrofurfuryl-alcohol  
 ketone keto alcohol (CO machine) : [ Acetone, ] 2-butanone, diacetone alcohol, gamma-butyrolactone, propylene-carbonate  
 carboxylic acid (CO machine) : [ Formic acid, ] An acetic acid, a propionic acid, a glycolic acid, a lactic acid, ethyl-lactate  
 nitroalkane (two NO(s)) : [ Nitromethane, ] A nitroethane, nitropropane, a nitrobenzene  
 amine (NR:R=H) ethylamine, Propylamine, an isopropylamine, a butylamine, an isobutyl amine, An allylamine, an aniline, a toluidine, ethylenediamine, a diethylamine, Ethyleneimine, a dipropyl amine, diisopropylamine, a dibutyl amine, A triethylamine, TORI n propylamine, and TORI n butylamine  
 acyl nitril (CN machine) : [ Acetonitrile, ] A propiononitrile, a butyronitrile, acrylonitrile, a methacrylonitrile, A benzonitrile  
 acid-amide (NR:R= alkyl group) formamide, N-methyl formamide, N,N-dimethylformamide, N-methyl acetamide, N, and N-dimethylacetamide, In a heterocyclic compound pyridine, a quinoline, a pyrrole, a piperidine, a piperazine, a morpholine, 2-pyrrolidinone, and a 1-methyl-2-pyrrolidinone this invention Surface treatment can be carried out by one sort of such an organic compound, or it can process being simultaneous or one by one with two or more sorts of organic compounds.

[0009] Moreover, the following can be used as an organic silicon compound used as the raw

material at the time of forming the aforementioned insulator layer by the chemical vapor deposition.

Tetrapod alkoxy silane (ortho silicate ester) : A tetramethoxy silane (TMOS), A tetrapod ethoxy silane (TEOS), tetrapod n propoxysilane, tetrapod isopropoxysilane, Tetrapod n butoxysilane alkyl-alkoxy silane : Methyl trimethoxysilane, Methyl triethoxysilane, MECHIRUTORI n propoxysilane, a methyl triisopropoxy silane, Ethyl trimethoxysilane, ethyltriethoxysilane, ECHIRUTORI n propoxysilane, An ethyl triisopropoxy silane, vinyltrimethoxysilane, vinyltriethoxysilane, Phenyl trimethoxysilane, dimethyl dimethoxysilane, dimethyl diethoxysilane, Diethyl dimethoxysilane, diethyl diethoxysilane, JIECHIRUJI n propoxysilane, Diethyl diisopropoxysilane, methyl vinyl dimethoxysilane, Methyl vinyl diethoxysilane, methyl dimethoxysilane, methyl diethoxysilane, Dimethyl vinyl methoxy silane and JIMECHIRUBINIRU ethoxy silane polysiloxane:tetrakis (dimethyl siloxy) silane cyclo SHIKISAN : Octamethylcyclotetrasiloxane (OMCTS), Pen reservoir chill cyclotetrasiloxane, tetramethyl cyclotetrasiloxane, A hexa methyl cyclotrisiloxane, trimethyl cyclotrisiloxane disiloxane : Hexa methyl disiloxane (HMDS), Tetramethyl dimethoxy disiloxane, dimethyltetramethoxydisiloxane, Hexamethoxydisiloxanealkylsilane : A monomethyl silane, dimethylsilane, A trimethyl silane, a triethyl silane, a tetramethylsilane, a tetraethyl silane, An allyl-compound trimethyl silane, hexa methyl disilane silylamine : Dimethyl trimethyl silylamine, Diethyl trimethylsilyl amine silane nitrogen derivative : Aminopropyl triethoxysilane, A trimethylsilyl azide, a trimethylsilyl cyanide silazane : A hexamethyldisilazane, Tetramethyl disilazane, an octamethyl cyclo tetrapod silazane, a hexa MECHIRUSHIKUROTORI silazane halogenation silane, and a derivative : A trimethylchlorosilane, A triethyl chlorosilane, a TORI n propyl chlorosilane, methyl dichlorosilane, A dimethyl chlorosilane, a chloro methyl dimethyl chlorosilane, a chloro methyl trimethyl silane, Chloropropyl methyl dichlorosilane, chloropropyl trimethoxysilane, A dimethyldichlorosilane, diethyl dichlorosilane, methyl vinyl dichlorosilane, A methyltrichlorosilane, an ethyl trichlorosilane, a vinyl trichlorosilane, To a truffe ROROPURO pill trichlorosilane, truffe ROROPURO pill trimethoxysilane, and a trimethylsilyliodide pan, as an organic silicon compound tris (trimethylsiloxy) A borane (start of block) and tris (trimethylsiloxy) The phosphoryl (SOP) and JIASETOKISHIJI-tert-butoxysilane (DADBS) etc. — it can use In this invention, the organic silicon compound mentioned above can be used independently, or two or more organic silicon compounds can be mixed and used. What is necessary is just to define suitably the mixed rate in the case of mixing and using.

[0010] Moreover, as the aforementioned surface treatment, the exposure processing by the steam of the application processing by the spin coater of the aforementioned organic compound, its solution, or its organic-solvent solution, immersing processing, the aforementioned organic compound, its solution, or its organic-solvent solution, spray processing, shower processing, curtain flow coat processing, etc. can be mentioned. It hits forming the insulator layer which acts as a layer insulation film of a semiconductor device in the suitable example of this invention, and is plasma CVD as a ground. Ordinary-pressure ozone which makes TEOS material gas after forming a TEOS NSG film and performing ethanol processing according the front face to a spin coater – CVD An AP O3-TEOS CVD NSG film is formed by the method.

[0011]

[Function] BURAZUMA CVD When forming the ground insulator layer to depend, as a result of setting the ratio of oxygen/TEOS as various values and performing experiment and examination, the membrane quality formed when the ratio is set or more to two has been improved further, and the good result was obtained. That is, if the ratio of oxygen/TEOS is set less than to two, the membrane quality of a plasma-TEOS CVD film will be bad, moreover carbide and water will contain, and an element property will also be bad.

[0012] Furthermore, if the ratio of oxygen/TEOS is set as two or more big values, since a silanol will be formed in the front face of the plasma-TEOS CVD film formed with high density, in the organic compound processing performed after that, an organic-solvent molecule adsorbs good, and almost all silanols are changed into Si-O-R. this alkylated silanol -- ozone-TEOS ordinary pressure CVD the time -- the front face of a ground film -- a character is made smooth, membrane quality is improved and embedded nature is raised remarkably therefore, plasma CVD forming an insulator layer in a ground insulator layer by the chemical vapor deposition, after

carrying out organic compound processing, while setting oxygen / TEOS ratio or more to two on the occasion of formation of the ground insulator layer to depend -- a front face -- while excelling in a character and membranous quality, it excels also in embedded nature, and the insulator layer by which generating of a void was prevented can be formed

[0013] Moreover, as a source of plasma used for plasma treatment, RF or the source of plasma of microwave can be used, and ammonia, nitrogen, hydrogen, oxygen, etc. can use these mixed gas as gas for plasma production. Especially the plasma of ammonia is very effective.

[0014]

[Example] Hereafter, with reference to a drawing, the example and the example of comparison of this invention are explained. Drawing 1 (a) And (b) It is the cross section showing the silicon substrate in a series of processes of the manufacture method of the semiconductor device by this invention. This example explains the example which forms an insulator layer on the 1st wiring. Drawing 1 (a) The BPSG film 12 whose thickness is 6000Å is formed on a silicon substrate 11 so that it may be shown, and it is a height of 1 micrometer on it further. It is line width 0.5 about the aluminum wiring 13.  $\mu\text{m}$  and space width 0.5  $\mu\text{m}$  It formed and the plasma-TEOS CVD NSG film 14 was formed after this BPSG film and aluminum wiring at the thickness of 3000Å. As membrane formation conditions for this plasma-TEOS CVD NSG film 14, they are 2.2Torr(s) about 400 \*\* and a membrane formation pressure in membrane formation temperature. It carries out and they are 200sccm(s) about TEOS. It supplied at a rate, oxygen gas was supplied at a rate of 4000sccm(s), a total of 1kW of 400kHz, 500W, and 13.56MHz and 500W was used as RF power, and membrane formation time was made into 20 seconds. Although the thickness of this plasma-TEOS CVD NSG film 14 is 3000Å on the aluminum wiring 13, about 1000-1500Å is formed in the side attachment wall.

[0015] Next, ethanol processing of the ground front face of this silicon base was carried out. In ethanol processing of this example, a silicon substrate is put on a spin coater, and it is 2000rpm. 2000rpm after applying ethyl alcohol for 3 seconds by the flow rate of 5 cc/min, making it rotate It was made to dry for 10 seconds. Next, it carries in in the reaction chamber which shows a silicon wafer, and is an ordinary pressure CVD. The ozone-TEOS CVD NSG film 15 was formed in 6000Å thickness on the following membrane formation conditions by the method. In addition, on these specifications, a quantity of gas flow shows the flow rate in the reference condition of 0 degree C and one atmospheric pressure.

[0016]

Membrane formation temperature 413 \*\* membrane formation pressure Nitrogen gas flow rate to an atmospheric pressure gas bubbler 1.7 SLM thermostat temperature Oxygen flow rate to 65 \*\* ozone generator 7.5 SLM ozone level 120 gNm<sup>-3</sup> carrier N2 quantity of gas flow 18 SLM [0017] Thus, the formed ozone-TEOS CVD NSG film 15 fills the narrow space during the aluminum wiring 13 smoothly, and has the good step coverage.

[0018] this invention is not limited only to the example mentioned above, but various deformation is possible for it. For example, although the example mentioned above explained the example which forms a TEOS CVD NSG film on aluminum wiring Organic silane CVD this invention can be applied when forming a film as a layer insulation film. Furthermore, it is formation and FET of the last passivation film. It can apply, in case a sidewall film is formed in the sides, such as a gate electrode, and in case a polysilicon contest multilayer interconnection is formed further, it can apply.

[0019] Furthermore, the metal which conductive wiring constitutes is not limited only to the example mentioned above, and can also use aluminum, Cu, Mo, W, Ti, TiN, TiW(s), or those alloys.

[0020] Furthermore, although the example mentioned above formed the ozone-TEOS CVD NSG film after performing ethanol processing, it can also form an ozone-TEOS CVDPSG film and a BPSG film by adding the phosphorus (trimethylborate) of TMOP (trimethylphosphate), TMB, etc., and the alkoxide gas of boron to the ozone supplied to a reaction chamber, and the mixed gas of TEOS as a dopant. furthermore, TMOS and OMCTS which were mentioned above not only in TEOS as an organic silane raw material compound, HMDS, start of block, DADBS, and SOP etc. -- it can also use

[0021]

[Effect of the Invention] As mentioned above, according to this invention, set the ratio of oxygen/TEOS or more to two, and a ground insulator layer is formed. Since it processes on a ground front face by the processing fluid containing an organic compound, an organic silane is used for it next and the insulator layer is formed in it by the chemical vapor deposition, while being able to raise membraneous quality further, a PARAZUMA-TEOS insulator layer The effect of organic compound processing can be raised further and the insulator layer which was further excellent in membraneous quality, embedded nature, and flat nature as a result can be formed.

---

[Translation done.]